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# The Influence of a Metastable Solid Phase on Eutectic Formation of a Binary Nematic Liquid Crystal

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The existence of a metastable solid phase of *p*-azoxyanisole (PAA) influences the phase diagram of binary mixtures of PAA and *p*-azoxyphenetole (PAP). In addition to a stable binary system having a eutectic transformation to a nematic phase at 97°C for a PAA mole-fraction ( $X_{\text{PAA}}$ ) of 0.59, a metastable binary (eutectic point at 86°C for  $X_{\text{PAA}} = 0.69$ ) is also observed. The Schröder-van Laar equations describe the phase diagrams of both systems well using reasonable values of the solid-nematic transition energies for the pure components.

## I INTRODUCTION

Para-azoxyanisole (PAA) is one of the most thoroughly studied liquid crystals. The thermal behavior has been investigated numerous times over the past 70 years.<sup>1-7</sup> Particularly related to the present work are the results of Chow and Martire,<sup>6</sup> who pointed out the existence of an apparently metastable solid phase of PAA, and of Hsu and Johnson,<sup>7</sup> who determined the phase diagram for a high-purity binary PAA/PAP system (previously studied by Prins,<sup>8</sup> Arnold and Sackmann,<sup>9</sup> and Schroeder, *et al.*<sup>10</sup>). Hsu and Johnson, however, did not observe the metastable phase for 100% PAA in their study (although their Figure 1 does show a small DSC peak which may correspond to a transition involving the metastable phase). It has been shown that the existence of a metastable solid phase can have an important influence on the phase behavior of a binary liquid crystal which forms a solid solution.<sup>11</sup> Therefore, the present work was undertaken to determine whether the metastable PAA phase could alter the phase diagram of PAA/PAP which

is known to form an eutectic.<sup>7</sup> As will be shown, two eutectic-forming systems can be found in this binary—one stable, the other metastable.

## II EXPERIMENTAL

Transition temperatures, heats of transition (latent heats) and sample purities were measured with a Perkin-Elmer DSC1B differential scanning calorimeter. The thermograms obtained were similar to those of Figure 1 in Ref. 7. Scan rates of 5°C/min were used, for the most part. The instrument was calibrated for both temperature and latent heat measurements using known standards. The temperature error is less than  $\pm 1^\circ\text{C}$ . Heats of transition were determined from peak areas in the usual manner.<sup>6,12</sup>

Samples of PAA and PAP were obtained from commercial sources and were used without further purification. Sample purities, determined from DSC scans,<sup>13,14</sup> were 99.0% and 99.3% for PAA and PAP, respectively. The impurity levels of our samples were, of course, considerably higher than those of the zone-refined samples of Hsu and Johnson,<sup>7</sup> and somewhat higher than that of the PAA studied by Chow and Martire<sup>6</sup> (99.7%). However, the purpose of the present work was to study the effect of a metastable phase, rather than to repeat the previous work on a high purity system.<sup>7</sup> Since there is some evidence<sup>15</sup> that a small amount of impurity may aid in the stabilization of the metastable PAA phase, there was no need for further purification of our samples. In any event, the thermal data of the present work is in reasonable agreement with that of the previous studies.

Mixtures were prepared by careful weighing of PAA and PAP into glass vials. The vials were capped, and the samples heated to the isotropic liquid phase and stirred. DSC samples were prepared by weighing  $\sim 5$  mg. quantities of the resulting mixtures into standard aluminum DSC pans, which were then hermetically sealed.

## III RESULTS

A summary and comparison of the thermal data for pure PAA and PAP are given in Table I. The latent heats of melting from the present work were corrected for “unobservable” pre-melting contributions in the usual manner.<sup>13,14</sup> This correction amounted to 6–8%. The agreement with previous data is adequate.

From Table I we see that for PAA the measured values of the latent heats of melting of the stable solid ( $\Delta H_{K_1N}$ ) range from 26.3 to 29.8 cal/gm (6800 to 7700 cal/mole); for the metastable solid the latent heat ( $\Delta H_{K_2N}$ ) range is 20.6 to 21.8 cal/gm (5330 to 5630 cal/mole). The range of measured latent

TABLE I  
Thermal data for PAA and PAP.

PAA	$T_{K_1N}(^{\circ}\text{C})$	$\Delta H_{K_1N}$ (cal/gm)	$T_{K_2N}(^{\circ}\text{C})$	$\Delta H_{K_2N}$ (cal/gm)	$T_{NI}(^{\circ}\text{C})$	$\Delta H_{NI}$ (cal/gm)	Ref.
	117.6	28.1	—	—	133.9	0.68	a
	118	29.8	—	—	132	0.68	b
	117	28.2	—	—	132	0.69	c
	118.2	27.4	—	—	135.3	0.64	d
	117.5	26.3	—	—	134.0	0.58	e
	117.5	28.1	104.4	21.8	134.2	0.70	f
	119.5	28.0	—	—	136.5	0.65	g
	119	27.8	104.5	20.6	133	0.59	h
PAP	$T_{KN}(^{\circ}\text{C})$	$\Delta H_{KN}$ (cal/gm)	$T_{NI}(^{\circ}\text{C})$	$\Delta H_{NI}$ (cal/gm)	Ref.		
	136.6	22.4	167.5	1.25	d		
	137.8	22.9	167.8	1.77	g		
	137	21.6	167.3	1.36	h		

<sup>a</sup> E. M. Barrall, R. S. Porter, and J. F. Johnson, *J. Phys. Chem.* **68**, 2810 (1964).

<sup>b</sup> R. Schenk, *Krystalline Flüssigkeiten u. Flüssige Kristalle*, W. Engelmann Verlag, (1905), pp. 84–89.

<sup>c</sup> H. Martin and F. Müller, *Kolloid z. u. z. für Polymere* **187**, No. 2, 107 (1963).

<sup>d</sup> H. Arnold, *Z. Physik. Chem. (Leipzig)* **226**, 146 (1964).

<sup>e</sup> M. Leclercq, J. Billard, and J. Jacques, *Compt. Rend.* **264**, 1789 (1967).

<sup>f</sup> L. E. Chow and D. E. Martire, *J. Phys. Chem.* **73**, 1127 (1969).

<sup>g</sup> E. Hsu and J. F. Johnson, *Mol. Cryst. Liq. Cryst.* **20**, 177 (1973).

<sup>h</sup> Present work.

heats ( $\Delta H_{KN}$ ) for PAP is 21.6 to 22.9 cal/gm (6190 to 6556 cal/mole). The uncorrected heats of melting from the present work were 26.0 (6450), 19.5 (5050), and 20.4 cal/gm (5850 cal/mole) respectively.

The observed behavior of mixtures containing sufficiently large quantities of PAA depends on the previous thermal history of the sample. A material cooled from the nematic mesophase may crystallize to the metastable solid with a eutectic temperature of  $\sim 86^{\circ}\text{C}$ . However, storage of the sample in the crystalline state for a sufficiently long time (several hours to one day) will ultimately yield the stable solid having a eutectic temperature of  $\sim 97^{\circ}\text{C}$ . That the solid with the  $86^{\circ}$  eutectic is metastable seems clear: it is well known<sup>16</sup> that if two polymorphic crystalline states melt to give the same liquid, the more stable one will have the higher melting point.

Figure 1 shows the phase diagram of binary mixtures of PAA and PAP. The behavior we found for the stable solid (indicated by  $\Delta$ ,  $\nabla$ ,  $\circ$ ) is essentially identical to that determined by Hsu and Johnson<sup>7</sup> (indicated by  $\blacktriangle$ ,  $\blacktriangledown$ ,  $\bullet$ ). The eutectic point for the stable system occurs at mole fraction

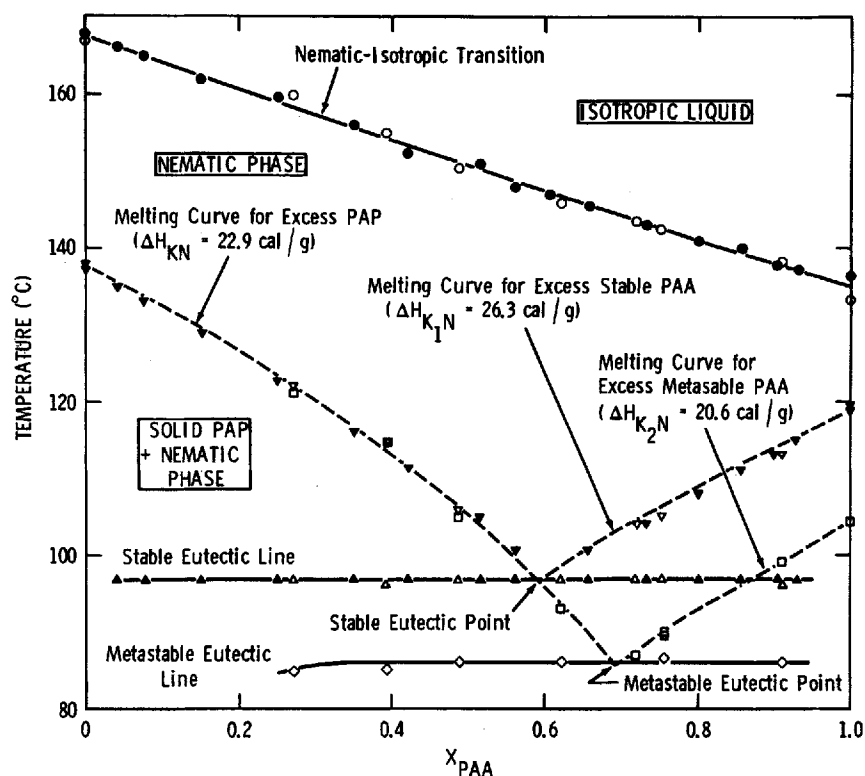


FIGURE 1 Phase diagrams of binary mixtures of PAA and PAP. Plotted are transition temperatures as a function of mole-fraction PAA,  $X_{PAA}$ . Solid points are data from Ref. 7 as follows:  $\blacktriangle$ -transition from stable crystal to two-phase region (melting of eutectic portion);  $\blacktriangledown$ -transition from two-phase region to nematic region (melting of excess component); and  $\bullet$ -transition from nematic to isotropic liquid. The open symbols ( $\triangle$ ,  $\nabla$ ,  $\circ$ ) are the corresponding results from the present work. In addition, data from the present work for transitions involving the metastable solid are represented by the following symbols:  $\diamond$ -transition from metastable solid to metastable two-phase region; and  $\square$ -transition from the metastable two-phase region to the nematic region. The solid curves are hand-drawn smooth fits to the data. The dashed curves are fits of the Schröder-van Laar equations for the indicated latent heats of the pure materials.

PAA ( $X_{PAA}$ ) equal to 0.59 and temperature equal to 97°C. At the eutectic temperature (for  $X_{PAA} \neq 0.59$ ) a transition to a two phase system (nematic plus excess solid component) is observed. To the left of the eutectic point the curve for the maximum melting temperature of excess component<sup>7</sup> (PAP) increases with decreasing  $X_{PAA}$ ; to the right the melting curve for excess stable PAA increases with increasing  $X_{PAA}$ .

When the metastable solid is formed (corresponding to a binary containing metastable solid PAA), a second eutectic point is found ( $X_{PAA} = 0.69$ ,

$T = 86^\circ\text{C}$ ). Our data for transitions involving the metastable system are indicated in Figure 1 by the symbols  $\diamond$  and  $\square$ . Apparently for compositions above  $X_{\text{PAA}} = 0.59$  and temperatures below the line for melting of excess stable PAA, the melting of excess metastable PAA yields the supercooled nematic phase. This conclusion was reached since no additional transitions were observed up to the nematic-isotropic transition temperature  $T_{NI}$  (indicated by data points  $\bullet$  and  $\circ$  in Figure 1). Of course, the magnitude of  $T_{NI}$  does not depend on whether the initial solid phase is the stable or metastable one.

The solid curves in Figure 1 are smooth, hand-drawn fits to  $T_{NI}$  and to the eutectic temperatures. Shown as dashed curves are plots of the Schröder-van Laar equations<sup>7</sup> for melting of the excess component to form the nematic:

$$\text{PAP-rich: } T = \frac{\Delta H_{KN} T_{KN}}{\Delta H_{KN} - RT_{KN} \ln(1 - X_{\text{PAA}})} \quad (1a)$$

$$\text{Stable, PAA-rich: } T = \frac{\Delta H_{K_1N} T_{K_1N}}{\Delta H_{K_1N} - RT_{K_1N} \ln X_{\text{PAA}}} \quad (1b)$$

$$\text{Metastable, PAA-rich: } T = \frac{\Delta H_{K_2N} T_{K_2N}}{\Delta H_{K_2N} - RT_{K_2N} \ln X_{\text{PAA}}} \quad (1c)$$

In these equations  $T$  is the transition temperature from the two-phase region to the nematic phase and  $R$  is the gas constant. (The temperature in Eqs. 1 is in degrees Kelvin.) The Schröder-van Laar curves in Figure 1 were calculated assuming the following values of the parameters:

$$\Delta H_{K_1N} = 26.3 \text{ cal/gm; } T_{K_1N} = 119^\circ\text{C (stable PAA)}$$

$$\Delta H_{K_2N} = 20.6 \text{ cal/gm; } T_{K_2N} = 104.4^\circ\text{C (metastable PAA)}$$

$$\Delta H_{KN} = 22.9 \text{ cal/gm; } T_{KN} = 137.8^\circ\text{C (PAP).}$$

Figure 2 shows the latent heats of melting of both the eutectic portion and the excess components of PAA/PAP binary mixtures. Data of both Hsu and Johnson<sup>7</sup> and the present work for the stable phase as well as our results for the metastable system are shown. No attempt was made to search for the metastable phase at concentration below  $X_{\text{PAA}} = 0.27$ . The solid curves in the figure are drawn through data for the eutectic and excess heats of transition for the stable system whereas the dashed curves represent the corresponding data for the metastable system.

Hsu and Johnson have also determined the nematic-isotropic transition energies  $\Delta H_{NI}$ . The values of  $\Delta H_{NI}$  from the present work are slightly smaller than those of Hsu and Johnson, but otherwise show similar behavior. Therefore, to avoid confusion, these data are not plotted in Figure 2.

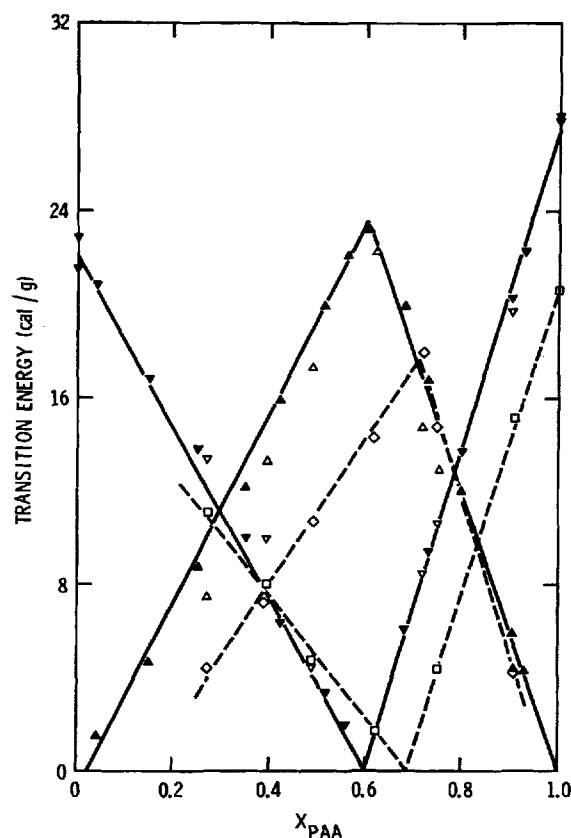


FIGURE 2 Transition energies of binary mixtures of PAA and PAP. Energies for melting of eutectic and excess component for both stable and metastable systems are plotted as a function of  $X_{PAA}$ . Symbols are as in Figure 1. Solid curves are drawn through data points for the stable system, dashed curves through points for the metastable one.

#### Discussion and conclusions

Several interesting observations emerge from this study. Most important, is the fact that, in a binary mixture of two nematogenic compounds, the existence of a metastable solid phase in one of them can lead to a metastable eutectic-forming one.

It is worth noting in the phase diagram of PAA/PAP (Figure 1) that for  $X_{PAA} < 0.69$  the temperature of transition from the two-phase metastable system to the nematic lies on the corresponding curve (or its extension) for the stable system. Similarly (Figure 2) for  $X_{PAA} > 0.7$  the transition energy of the metastable eutectic component is essentially equal to that for the stable eutectic component of the same composition.

The error in determining  $\Delta H$  in our experiments was somewhat larger than that in determining  $T$  because of difficulties in completely resolving the eutectic and excess component peaks for certain compositions. Hence the eutectic compositions in Figure 2 do not agree exactly with those of Figure 1. However, the agreement is within 1%.

The Schröder-van Laar equations fit the excess component melting curves very well using appropriate values of crystal-nematic transition energies from Table I. The best fit for the stable-phase PAA-rich region was obtained using the smallest value of  $\Delta H_{K1N}$  in the table. However, the fit is not extremely sensitive to  $\Delta H$ . For example, changing  $\Delta H_{K1N}$  from 26.3 to 28.0 cal/gm and  $T_{K1N}$  from 119°C to 119.5°C shifts the eutectic point only from  $X_{PAA} = 0.59$ ,  $T = 96.7^\circ\text{C}$  to  $X_{PAA} = 0.58$ ,  $T = 97.7^\circ\text{C}$ . This latter eutectic point, which is calculated with the parameters of Ref. 7, disagrees with that calculated by Hsu and Johnson ( $X_{PAA} = 0.59$ ,  $T = 96.6^\circ\text{C}$ ). The reason for the discrepancy, however, is not clear.

Based upon the results of this initial study, a more detailed investigation of the influence of metastable solid phases on binary or multiple mixtures of nematic liquid crystals will be needed for a complete understanding of mixed mesomorphic materials. Certainly such an understanding is important for applications of extended-range nematics to devices operating at low temperatures.

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